Neutron Activation for Distinguishing Cascade Range Pyroclastics

Abstract. *Neutron activation of glassy separates of volcanic ash resulted in 21 nuclides measurable with instrumental techniques. The relative activities of most of the nuclides distinguish samples from Mount Mazama, Newberry Crater, and Glacier Peak. The usefulness of the technique was assessed by comparing the values for known sources with those from fine ash of uncertain origin. The data strongly suggest Mount Mazama as the source.*

Volcanic ash layers may be used as stratigraphic horizon markers, but this approach depends upon the ability to distinguish different ash deposits. One of the principal sources of volcanic ash in Oregon was an eruption of Mt. Mazama about 6600 years ago (*1*). Another major source of volcanic ash in the Pacific Northwest was Glacier Peak, with an eruption about 12,000 years ago (*2*). Material from both of these sources may occur in northeastern Oregon (*2*). In certain areas, they can be further confused with materials from Newberry Crater, Mt. St. Helens, and Mt. Rainier. An investigation is in progress to determine the mineralogy and weathering products across a transect of soils from Mazama pumice and ash. It is, therefore, necessary to determine that the selected sample sites do indeed represent Mazama pyroclastics.

Glacier Peak and Mazama pyroclastics have been distinguished previously on the basis of mineralogy, major element composition, and index of refraction (*3, 4*). Titanium dioxide contents were used with some success to distinguish between a majority of Glacier Peak and Mazama ash samples (*5*). Overlap in such parameters and bimodal frequency distributions sometimes hinder unequivocal distinctions between the deposits. Neutron activation analysis has been successfully applied to rocks and meteorites (*6, 7*). The method has the advantage of providing a large number of trace element abundances which can be used to increase the reliability for distinguishing samples. We therefore began an investigation of the merits of instrumental neutron activation analysis to discriminate between ash deposits. This report presents the results of preliminary studies. Specifically, it outlines what elements can be determined in volcanic glass, what relative differences are obtained for samples from different sources, some of the methods and problems, and an assessment of the technique.

Mazama pumice was sampled northwest of China Hat in Deschutes County, Oregon (Sec. 9, T22S, R14E, Willamette Meridian). An upper coarse layer (I) and a finer-textured lower layer (II) can be distinguished in Mazama pumice at this and other locations. Samples from both layers were obtained. The textural differences between layers I and II of Mazama ash reflect the increasing violence of later eruptions of Mt. Mazama (*8*). Newberry Crater pumice overlying Mazama pumice with an abrupt, smooth boundary was obtained at the same location. Volcanic ash from Glacier Peak was sampled in Steptoe Canyon in southwestern Washington [previously described by Fryxell (*2, 9*)].

Fractions the size of fine sand (125 to 63 μ) were sieved from bulk samples of pumice and volcanic ash. Contamination of layers of pyroclastics by primary minerals and possible differences due to mineral sorting might contribute to geochemical variability and confound the interpretations. Glassy components, therefore, were isolated from the sieved fractions with bromoform-bromobenzene, $\rho = 2.4$ g/cm^3. Contamination of trace elements from the bromoform-bromobenzene separation was found to be negligible. The success of the separation was checked on the Mazama ash sample. About 80 percent of the sieve fraction had a density less than 2.4 g/cm^3. Crystal inclusions occurring within the glassy separate were less than 5 percent of the sample. We subsequently determined that for soils, an additional separation at 2.2 g/cm^3 removes dark fragments that appear to be plant residues.

The method of instrumental neutron activation analysis has been demonstrated by Schmitt *et al.* (*6*) with NaI(Tl) detectors and by Gordon *et al.* (*7*) with Ge(Li) detectors. We used the method of Gordon *et al.* (*7*) except that the counting equipment consisted of a 3.6-cm^3 Ge(Li) semiconductor detector and 4096 Nuclear Data Multichannel analyzer. Contributions of the low-energy peaks of Fe, Yb, and Eu activities were subtracted from the peaks of Ce, Pa(Th), and Tb, respectively (*10*). Quantitative estimates of the abundances of the 21 elements found were obtained by comparison with similarly activated standard solutions of the elements. Final calibrations of standard solutions are being completed and, therefore, the concentrations given for Mazama ash, layer I,

Table 1. Approximate elemental abundances in Mazama ash (layer I) and relationship to activities found for samples of volcanic ash from Mazama layer II, Newberry Crater, and Glacier Peak.

Element	Mazama (layer I) (ppm)*	Ratios		
		Mazama II/ Mazama I	Newberry/ Mazama I	Glacier Peak/ Mazama I
Sm	5.21 ± 0.18†	1.21 ± 0.05†	1.66 ± 0.07†	0.45 ± 0.02†
Fe (%)	2.93 ± .12	1.29 ± .05	0.60 ± .03	.69 ± .03
Sc	13.3 ± .30	1.27 ± .05	.69 ± .03	.53 ± .02
Ta	0.46 ± .01	1.14 ± .07	2.00 ± .09	.52 ± .05
Na (%)	3.41 ± .24	1.13 ± .08	1.45 ± .11	.75 ± .06
Co	9.5 ± .9	1.26 ± .08	0.36 ± .04	.84 ± .06
Ce	45.1 ± 2.7	1.26 ± .10	1.68 ± .08	.56 ± .05
Mn	450 ± 16	1.03 ± .10	0.92 ± .10	.64 ± .06
Eu	1.21 ± 0.15	1.27 ± 0.23	0.74 ± 0.19	0.60 ± 0.14
Nd	15.7 ± 2.7	1.23 ± .25	1.22 ± .25	.58 ± .14
La	25.7 ± 5.7	1.07 ± .34	1.76 ± .44	.61 ± .21
Lu	0.55 ± 0.12	1.09 ± .21	1.47 ± .42	.42 ± .38
Th	7.7 ± 1.8	1.00 ± .63	1.64 ± .47	.56 ± .50
Yb	3.20 ± 0.21	1.26 ± 0.75	1.65 ± 0.65	0.21 ± 0.22
Cr	17.0 ± 9.0	1.84 ± 1.06	0.61 ± .58	.29 ± .29
Cs	3.9 ± 1.8	1.02 ± 0.48	1.02 ± .39	.51 ± .34
Ba	837 ± 420	0.98 ± .59	0.99 ± .61	.26 ± .41
Hf	6.0 ± 3.3	1.03 ± .64	1.90 ± 1.20	.37 ± .23
Dy	5.7 ± 3.0	1.12 ± .77	1.43 ± 0.89	.51 ± .39
Rb	39 ± 30	1.32 ± 1.35	1.80 ± 1.50	1.87 ± 1.77
Tb	0.9 ± 0.9	0.89 ± 1.18	0.95 ± 0.39	0.40 ± 0.82
Mean ratio, $\bar{X}$		1.18	1.26	0.58
Coefficient of variation		16%	38%	56%

* Elemental abundances are in parts per million, except iron and sodium, which are in percent.
† Three standard deviations based on counting statistics.

Table 2. Activity ratios for two soil samples. Abbreviations: O.V.P., Ochoco View Point; $\overline{X}$, mean ratio; C.V., coefficient of variation.

Element	O.V.P. AC2/ Mazama I	Whisky Flat AC2/ Mazama I
Sm	0.85 ± 0.04*	0.73 ± 0.05*
Fe	.85 ± .05	1.01 ± .04
Sc	.80 ± .04	1.00 ± .04
Ta	.71 ± .07	0.72 ± .06
Na	.97 ± .09	.94 ± .09
Co	.86 ± .09	1.11 ± .09
Ce	1.15 ± .08	1.01 ± .08
Mn†	2.26 ± .20	1.57 ± .14
Eu	0.97 ± 0.23	0.91 ± 0.20
Nd	1.20 ± .23	.82 ± .16
La	1.22 ± .32	1.10 ± .23
Lu	0.85 ± .44	0.66 ± .26
Th	1.10 ± .32	1.01 ± .37
Yb	0.79 ± 0.49	0.83 ± 0.41
Cr	.89 ± .45	1.50 ± .76
Cs	.67 ± .48	0.88 ± .58
Ba	1.23 ± .96	.89 ± .65
Hf	0.52 ± .44	.84 ± .53
Dy	.87 ± .87	.77 ± .64
Rb	1.14 ± 1.25	1.09 ± 1.17
Tb	0.70 ± 1.28	0.47 ± 0.87
$\overline{X}$	0.92	0.91
C.V.	21%	23%

* Three standard deviations based on counting statistics. † The values for Mn are not included in mean and C.V.

are to be regarded as preliminary (Table 1). The first group of elements could be determined the most accurately and the last group was determined with the least accuracy. The precision of the results is estimated from counting statistics using three standard deviations. Refinements of technique in future analyses will include the use of a 30-cm^3 Ge(Li) crystal rather than the 3.6-cm^3 crystal with which these data were obtained. Use of a 30-cm^3 crystal will considerably increase the precision of determinations.

Since the question we are dealing with concerns the ability to distinguish between different samples, the absolute levels are less important than relative differences. Activities of the nuclides in the different ash samples were compared with the activities found for Mazama (I) by using the ratio [$A^o(x)$ for sample of unknown]/[$A^o(x)$ for Mazuma (I),], where $A^o(x)$ is the counts per minute per gram of sample for the nuclide formed from element x (Table 1). For Mazama (I) samples, the activity ratio for a given element should be 1 by definition. The mean ratio for all elements in the sample should also be 1 and the coefficient of variation should be low (*12*). Low coefficients of variation (based upon all activity ratios) are a measure of the similarity to Mazama (I). Relative to Mazama layer I, the elemental abundances generally were higher in samples from Mazama layer II, mean ratio 1.18, and Newberry, mean ratio 1.26. The Glacier Peak sample yields much lower activity ratios with a mean value of 0.58. The coefficient of variation for Mazama II (16 percent) contrasts with Newberry (38 percent) and Glacier Peak (56 percent) as expected for samples unrelated to Mazama. Although the mean ratios and coefficients of variation are informative, the ratios for individual elements are of interest. The compositions of particular elements are expected to be of use for discrimination. Relative to Mazama (I), the Newberry sample is significantly higher in Sm, Ta, Na, Ce, La, and Th; it is lower in Fe, Sc, and Co. Contents of most elements in the Glacier Peak sample are lower than for Mazama (I).

Table 3. Elements whose activity ratios are within three standard deviations of ratios for the known materials.

Source	Ochoco View Point AC2 horizon	Whisky Flat AC2 horizon
Mazama	Na, Co, Nd, La, Ce	Na*, Fe*, Sc*, Ce*, Eu, Co, La, Yb, Lu
Newberry Crater	Nd, La, Ce	La, Yb
Glacier Peak	Co	Lu

* Ratios for these elements are within the range for layer I. Other elements listed under "Mazama" have ratios within the ranges of both Mazama layer I and layer II.

We desire to extend the findings obtained on coarse pumice of known origin to the identification of fine ash deposits of uncertain origin encountered at considerable distance from possible sources. An assessment of the technique was made by comparing the values of known materials with those from two ashy soils of uncertain origin. One soil developed from volcanic ash was sampled at Ochoco Viewpoint in the Ochoco National Forest, Crook County, Oregon (Sec. 28, T12S, R19E). Another soil was sampled at Whisky Flat in the Malheur National Forest, Grant County, Oregon (Sec. 20, T10S, R32E). Glassy fractions were iolated from 125- to 63-μ fractions of AC2 soil horizons and analyzed as previously described.

Activity ratios (relative to the Mazama I sample) for the Ochoco View Point and Whisky Flat soil samples averaged 0.92 and 0.91 with coefficients of variation of 21 and 23 percent, respectively (Table 2). The soil samples also were compared to the Newberry and Glacier Peak samples by calculation of appropriate activity ratios. Relative to Newberry, the Ochoco Viewpoint sample has a mean ratio of 0.87, but the coefficient of variation is 56 percent. The Whisky Flat sample has a mean ratio of 0.72, but the coefficient of variation is 75 percent. Relative to Glacier Peak, the Ochoco Viewpoint sample has a mean ratio of 1.94 and a coefficient of variation of 48 percent. The Whisky Flat sample has a mean ratio of 1.93 and a coefficient of variation of 54 percent.

Manganese was not included in the above averages since the enrichment of Mn is thought to result from MnO$_2$ coatings or concretionary forms in the soil. One of the soil samples was subsequently treated with sodium dithionite-citrate (*11*). This treatment yielded Mn contents in general agreement with the Mazama I sample. However, the addition of reagents to a sample always presents some chance of adding other contaminants to the system. Until these effects and purity of reagents are determined, we prefer to omit the analyses for Mn.

The activity ratios for some of the more accurately determined individual elements provide further information as to probable source of volcanic ash for the two soils (Table 3). More of the elements for the soil samples have ratios overlapping the ratios for Mazama than for Newberry or Glacier Peak. The data in Tables 2 and 3 strongly suggest Mazama as the source of volcanic ash for these soils.

The primary purpose of this study was to determine the potential usefulness of instrumental neutron activation analysis for distinguishing different volcanic materials. We conclude that neutron activation analysis is a very promising technique for the characterization of pumice from different sources and for the correlation of volcanic ash soils. Further refinements are necessary. Greater precision in counting statistics is desired. This should be obtained with other crystal detectors. For correlation work, it is necessary to have reliable estimates of confidence limits for elemental abundances in the different deposits. The data presented here are not necessarily intended to characterize the deposits. The confidence limits for a given material should include sampling and deposit variability as well as counting statistics.

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Antarctic Ice Sheet: Preliminary Results of First Core Hole to Bedrock

Abstract. *The Antarctic ice sheet at Byrd Station has been core-drilled to bedrock; the vertical thickness of the ice is 2164 meters. Liquid water—indicative of pressure melting—was encountered at the bed. Heat flow through the base of the ice sheet is estimated at 1.8 microcalories per square centimeter per second. The minimum temperature was − 28.8°C at 800 meters; maximum ice density, 0.9206 at 1000 meters. Core studies reveal the existence of a chemically pure, structurally stratified sheet comprising bubbly ice to 900 meters that transforms to bubble-free deformed ice, with substantially vertically orientated* c*-axis structure, below 1200 meters. Below 1800 meters the deformed ice structure gives way to large annealed crystals. Several thin layers of dirt between 1300 and 1700 meters are tentatively identified as volcanic ash, and horizontally banded debris, including fragments of granite, is present in the basal ice.*

On 29 January 1968 the first core hole to penetrate the bottom of the Antarctic ice sheet was drilled (*1*) at Byrd Station (80°01′S, 119°31′W; elevation, 1530 m) (Fig. 1). The vertical thickness of ice was 2164 m and more than 99 percent of the core was recovered. Cores were sought for investigations of the physical properties of the ice sheet, the nature of the ice-rock contact, and the composition of the underlying bedrock. Temperatures and deformation in the ice sheet are measured in the drill hole which will be used also for large-scale extraction of the englacial air required for radiocarbon dating of the ice sheet (see *2*).

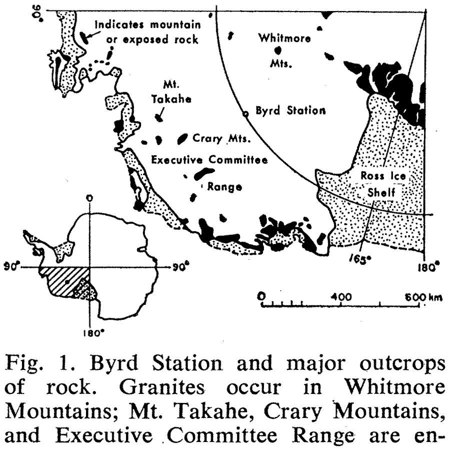

Fig. 1. Byrd Station and major outcrops of rock. Granites occur in Whitmore Mountains; Mt. Takahe, Crary Mountains, and Executive Committee Range are entirely volcanic.

Drilling was accomplished with a cable-suspended electromechanical rotary drill (*3*) that had been modified for coring in ice and had been tested in Greenland (*4*). The drill, driven by a 17.5-hp induction motor, was 26.5 m long, and weighed 1100 kg, and could be reeled in and out of the hole at a maximum rate of 46 m/min.

Drill cuttings were dissolved in ethylene glycol which was bailed after each coring run. The hole was cased to a depth of 88.4 m with 17.8-cm steel casing to prevent hole fluid from leaking into the permeable layer of firn. This fluid, a mixture of arctic diesel oil and trichlorethylene of the same density as ice (0.92), is required in the hole to prevent closure by plastic flow of the ice.

Cores 3 to 6 m in length and averaging 10.8 cm in diameter were recovered from the 16.2-cm hole. Drilling rates varied from 3.3 to 19.8 cm/min, the overall rate of coring averaging 20 m/day. The hole began to deviate from the vertical at 320-m depth, and the inclination had increased to 15 deg before bottom was reached.

Ice temperatures (Fig. 2), measured with a thermistor-type probe after completion of the drilling, are accurate within 0.1°C. Measurements of temperature below 1800 m were prevented by an accumulation of slush that could not be bailed before the end of the season. The minimum temperature was − 28.8°C at 800 m; the temperature at 1800 m was −13.0°C, and the pressure-melting point of the ice at the bottom, where the load pressure was 197 bars, was estimated at − 1.6°C. Extrapolating the temperature curve below 1800 m gives a temperature gradient of 3.25°C/100 m. Using an average ice temperature of −9.0°C in this region and Ratcliffe's (*5*) data for the thermal conductivity of ice, the basal heat flow is calculated at 1.8 μcal cm^{-2} sec^{-1}. An unknown proportion of this heat may be due to the flow of the ice.

Bedrock beneath the ice sheet was penetrated to a depth of 1.3 m, but a core could not be retrieved for reasons that remain uncertain; perhaps the material is unconsolidated sediment, such as glacial till, rather than solid rock. Glacial till underlies the Greenland ice sheet at Camp Century (*4*).

Liquid water was encountered at the ice-rock interface, clear evidence that the bottom of the ice sheet is at the pressure-melting point. Because of a slight deficiency in the density of the hole liquid, the bottom water flooded the hole to a height of about 50 m. Preliminary calculations indicate that this water was derived from a layer of water at least 1 mm thick.

Apart from very brittle and badly fractured sections from between 400 and 900 m, the overall condition of the core varied from good to excellent. Dirt was abundant in the bottom 4 to 5 m of core, including bands of silt, sand, and pebbles, with scattered larger fragments—all interspersed with ice. Pending detailed analysis of these cores it was noted that the largest fragments

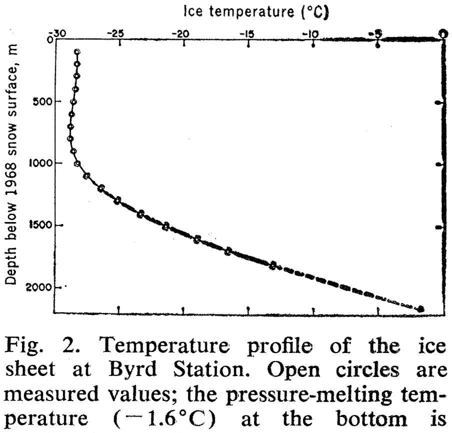

Fig. 2. Temperature profile of the ice sheet at Byrd Station. Open circles are measured values; the pressure-melting temperature (−1.6°C) at the bottom is marked by a solid circle.